PARTITIONING OF HYDROGEN IN THE VANADIUM-LITHIUM-HYDROGEN
SYSTEM AT ELEVATED TEMPERATURES*

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ABSTRACT

Equilibrium concentrations of hydrogen in vanadium-base alloys exposed to flowing lithium at temperatures from 350 to 550° C in a forced-circulation loop were measured by residual gas analysis and the vacuum fusion method. Residual gas analysis and removal of material from the surface allowed a determination of the spatial hydrogen distribution in the alloys. These experimental results were compared with calculated thermodynamic distribution coefficients for hydrogen in the vanadium/lithium system. Small amounts of other solutes in the molten lithium and in the alloys affected the solubility, diffusivity, and resultant distribution of hydrogen. Thermodynamic calculations demonstrated the importance of major alloying elements to the partitioning of hydrogen.

I. INTRODUCTION

Vanadium alloys such as V-15Cr-5Ti, V-7.5Cr-15Ti, and V-3Ti-1Si are attractive candidates for use as structural materials in fusion reactor blankets because of their excellent resistance to neutron radiation damage, low induced radioactivity, high strength at elevated temperatures, and favorable thermophysical properties.

Molten lithium has been proposed as both a coolant and breeder material because of its excellent heat transfer and tritium breeding characteristics. Local corrosion phenomena and mass- and interstitial-element transfer rates depend on the difference between the chemical activity of the alloy constituents and that of lithium and the structural material.

Understanding the parameters that affect the solubility and diffusivity of tritium in liquid lithium is important for evaluating the permeation and inventory of tritium in the blanket

and optimizing the tritium extraction process. Additionally, the issue of hydrogen-isotope induced embrittlement is a major question for all structural alloys exposed to the neutron environment expected in a fusion reactor.

II. EXPERIMENTAL PROCEDURE

A. Lithium Test Facility

The hydrogen distribution tests were conducted in a forced-circulation lithium loop. The liquid lithium system, which was constructed of Type 304 stainless steel, consisted of a primary loop equipped with three test vessels and a secondary cold-trap purification system. A more detailed description of the lithium test facility has been presented previously.¹ The quantity of lithium in the loop was ~20 l, and the lithium in the primary loop was recirculated at ~ 1 l/min. from the high-temperature to the low-temperature test vessel. The cold-trap temperature was maintained at ~210° C (31° above the freezing temperature of lithium). Hot trapping with titanium or zirconium foils (or dissolved getters) was used to maintain the nitrogen level to under ~50 wppm in the lithium, which was considerably below that attainable by cold trapping. Other interstitial elements in lithium were also regulated in this manner. Hydrogen partial pressure (P_{H_2}) was monitored daily. Filtered (5 μ metal frits) lithium samples were analyzed for nitrogen and carbon. The procedure for lithium sampling has been described in detail elsewhere.²

B. Measurement of Hydrogen Pickup by Vanadium Alloys

Specimens of V-15Cr-5Ti and V-3Ti-0.5Si were immersed in the flowing lithium in two separate isothermal test vessels maintained at different temperatures. The specimens had approximate dimensions of 1.9 cm x 1.0 cm x 0.09 cm and were mechanically polished before exposure to lithium. Following exposure, the specimens were cleaned in methanol to avoid the introduction of hydrogen.

Total hydrogen in the specimens after exposure to the lithium was determined from the P_{H_2} in the gaseous constituents that were evolved on heating a specimen at a rate of 15°C/min from 25°C to 1000°C. The P_{H_2} was determined by use of a quadrapole, partial-pressure, residual gas analyzer (RGA) mounted in an ion-pumped vacuum system. The temperature of a specimen during heating was determined with a recording infrared pyrometer. The hydrogen concentration in the lithium-exposed specimens was also determined by the combustion technique in a LECO Model RH-1 Hydrogen Determinator. The measurement technique was calibrated with NBS standards.

C. Measurement of the Partial Pressure of Hydrogen in Lithium

The hydrogen partial pressure in lithium was measured by use of a hydrogen activity meter. The original design of the meter, previously used in sodium test facilities,³ contained four thin-walled nickel tubes (of about 0.3" O.D. and 0.28" I.D.) across which there was a pressure gradient of about 20 psi; an ion pump; and an evacuated chamber. In the modified design for the lithium test facility, hydrogen permeated through a sensor consisting of an alpha-iron membrane immersed in liquid lithium in the supply vessel. The ion pump was valved out and the hydrogen was allowed to diffuse into the manifold until equilibrium was attained. The equilibrium pressure was measured with a dual range ionization gauge.

III. RESULTS

A. Hydrogen in Lithium

Lithium hydride, LiH, is the solid phase in equilibrium with saturated solutions of hydrogen in lithium. The temperature dependence of the terminal solubility, S_H , expressed in weight fraction, is given by the following equation⁴

$$\ln S_H = 1.578 - 5314/T \quad (1)$$

where T is the absolute temperature. Although small variations for the constants in Eq. 1 have been reported,⁵ Eq. 1 was considered to be an acceptable relationship between temperature and terminal solubility. As can be seen in Fig. 1, the calculated solubility of hydrogen in lithium increases uniformly with increasing temperature.

In metals, hydrogen gas dissolves in atomic form. The relationship between the concentration of hydrogen in solution and P_{H_2} can be represented by Sieverts' constant, K_S , as follows:

$$C = K_S (P_{H_2})^{1/2} \quad (2)$$

where P_{H_2} is expressed in torr and C is the weight fraction of hydrogen in the lithium.

The temperature dependence of the Sievert's constant, K_S , is expressed as

$$\ln K_S = A + B/T \quad (3)$$

The values of the constants A and B for hydrogen in lithium and various refractory metals have been determined and are given in Table 1.

To a first approximation, the lithium-hydrogen system is in equilibrium and the value of C in Eq. 2 will approach that of S_H . Subsequently, P_{H_2-T} , the temperature-dependent pressure based on Sievert's Equation, can be calculated from Eq. 2, substituting in S_H from

Eq. 1 with the absolute temperature of the cold trap and K_S from Eq. 3 with the absolute temperature of the supply vessel. The P_{gauge} is measured by a pressure sensor connected to the hydrogen activity meter. The magnitude of the pressure readings must then be calibrated to the actual hydrogen partial pressure. Data from 232 pressure gauge readings taken over a period of ~3 yr were plotted against the calculated partial pressure, P_{H_2-T} , corresponding to the same temperatures of cold trap and supply vessel. A linear least squares fit to these 232 data points was used to derive a calibration equation for the normalized hydrogen partial pressure, P_{H_2-N} , of

$$P_{H_2-N} = -0.16583 + 0.10566 P_{gauge} \quad (4)$$

Subsequently, by substituting P_{H_2-N} into Eq. (2), and using Eq. (3) to determine K_S , we could derive the dissolved concentration of hydrogen in lithium, C_N , from the normalized partial pressure and the temperatures of the cold trap and the lithium supply vessel where the pressure sensor was immersed. In Fig. 2, such results (closed diamonds) are compared with the solubility, S_H , determined by Eq. (1). Similarly, the theoretically derived values for the partial pressure, P_{H_2-T} , are compared with the gauge-derived values, P_{H_2-N} , as obtained in Eq. (4).

The temperature of the supply vessel and cold trap at the top of Fig. 2 can be seen to have an effect on both the measured and calculated values for hydrogen in lithium. A case in point is for $t = 5.07 \times 10^4$ h (the loop age of this batch of lithium at the time of the gauge reading) where the cold trap temperature drops 16° C and concentrations plummet. These events are further evidence that the concentration of hydrogen in lithium can be considered to be controlled by the temperature of the cold trap.

B. PARTITIONING OF HYDROGEN

Hydrogen will fractionate between lithium and various refractory metals as a function of temperature. A distribution coefficient, K_W , can be defined as the ratio of the hydrogen concentration in the metallic alloy to that in the liquid lithium:

$$K_W = C_M / C_{Li} \quad (5)$$

where C_M and C_{Li} are concentrations (wt%) of hydrogen in the metal and lithium, respectively, at constant P_{H_2} . Temperature-dependent distribution coefficient equations for hydrogen between lithium and several refractory metals take the same form as Eq. (3) and the parameters A_1 and B_1 are tabulated in Table 1. Using these tabulated values for A_1 and B_1 , coefficients describing the distribution of hydrogen among various refractory metals and liquid lithium are shown graphically in Fig. 3 as a function of temperature. At a temperature of 500° C, a hydrogen concentration of 100 wppm in lithium will establish a calculated hydrogen concentration of ~3000 wppm in yttrium, 10 wppm in titanium, 0.3 wppm in vanadium, and < 0.0001 wppm in chromium.

The sign and size of the enthalpy of solution is the governing parameter controlling how much hydrogen is absorbed by a metal.¹⁰ The solubility of hydrogen is highest in yttrium which has the most negative enthalpy of solution. This property, also reflected in the distribution coefficient equation, can be utilized to provide an independent determination of the concentration of hydrogen in the lithium and can be used, not only to calibrate the meter, but also as an additional check on the accuracy of the calibration equation, Eq. (4).

Yttrium samples were exposed to lithium in the loop at temperatures ranging from 408 to 538° C. The concentration of hydrogen in the yttrium specimens, determined by vacuum fusion analysis (Table 2), was used in conjunction with calculated distribution coefficients to determine the hydrogen concentration in lithium. The concentrations are plotted as a function of cold trap temperature (Fig. 1). The results show that, to a first approximation, the cold-trap temperature had a significant effect in controlling the upper limit of hydrogen in the system. As can be seen in Fig. 1, the hydrogen concentrations determined by yttrium exposure show good agreement with the solubility curve.^{4,5} On the basis of comparisons of the hydrogen concentrations obtained from equilibrations of yttrium foils, the hydrogen probe gave an acceptable correlation between the measured partial pressure and the hydrogen content of the lithium.

Work is currently being done to determine the distribution coefficients for hydrogen between vanadium alloys and liquid lithium (Fig. 3). The distribution coefficients for both V-15Cr-5Ti and V-3Ti-0.5Si (hydrogen determined by RGA) are higher than those predicted from the thermodynamically derived equation for hydrogen distribution between vanadium and lithium (Table 1).

Figure 4 summarizes results of hydrogen analyses of different vanadium alloys after exposure to lithium at different hydrogen activities. Since the concentration of hydrogen in lithium at lower temperatures approximates the solubility values (open circles in Fig. 1), these values can be used to estimate the hydrogen concentration in the pure metals (V, Ti, Cr) by means of the distribution coefficient relationship, Eq. (5). The upper curve represents a

theoretical value for hydrogen in titanium; the lower curve depicts the hydrogen in pure vanadium. The hydrogen concentration in the V-3Ti-0.5Si alloy is higher than that in the V-15Cr-5Ti alloy, as would be expected from the distribution coefficient relationships graphically represented in Fig. 3.

As shown in Fig. 4, the equilibrium concentrations of hydrogen in candidate vanadium alloys exposed to a flowing lithium environment in a forced-circulation loop were measured at 400 and 500 °C by an RGA method. The RGA, coupled with removal of material from the surface, allowed a determination of the spatial hydrogen distribution in the vanadium alloys. This is qualitatively represented in Fig. 5, which depicts the evolution of hydrogen from the surface as a function of time. Since the specimens were heated in the furnace at a rate of 15° C/min, this can be related via the diffusion coefficient to the depth where hydrogen occurred. It was observed that the corrosion product layer formed on V-3Ti-0.5 Si after lithium exposure contained a large fraction of the total hydrogen in the specimen. As would be anticipated from the distribution coefficients for the component elements in these alloys (Fig. 3), the concentration of hydrogen in the examined vanadium alloys decreased after exposure to lithium.

IV. DISCUSSION

An equation has been developed for a normalized partial pressure based on hydrogen activity meter gauge readings. The hydrogen concentrations determined both by calculations originating from these normalized partial pressures and by calculations originating from yttrium exposures show good agreement with the hydrogen solubility curve.

As in an earlier study of the distribution of hydrogen between vanadium alloys and lithium,² it was observed that the measured hydrogen concentrations in the alloys were significantly higher than those calculated from the distribution coefficient, and that the hydrogen concentration in the V-15Cr-5Ti alloy was substantially greater than that predicted in the pure vanadium. As can be seen in Fig. 4, this can be attributed to the presence of titanium which has a higher expected concentration of hydrogen. It has been observed¹¹ that the solubility and diffusion of hydrogen in vanadium are influenced by the presence of small amounts of other alloying elements. In general, an increase in the hydrogen solubility and a decrease in the hydrogen diffusivity with increasing substitutional concentrations have been reported. Titanium increases the solubility of hydrogen in vanadium, whereas chromium may decrease or not affect the solubility. Similarly, the diffusion coefficient for hydrogen in vanadium decreases with the addition of titanium, whereas chromium has no effect. Trapping of hydrogen atoms at lattice imperfections, e.g., dislocations, interstitial impurities, and

substitutional alloying atoms, has often been discussed as an explanation for these observations¹¹.

Since the distribution coefficient for hydrogen in vanadium is much less than one ($\sim 10^{-2}$), hydrogen embrittlement as a result of a higher concentration in lithium would not be expected. Since the tritium concentration in a vanadium alloy fusion reactor structural material is expected to be maintained at less than 1% of that in our lithium loop (<1 wppm),¹² the results obtained in this study indicate that tritium pickup by vanadium alloys in the reactor structure will not be significant.

V. ACKNOWLEDGMENTS

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Table 1. Values for Parameters A and B in Distribution Coefficient Equations and Sievert's Constant Equations of the Form $\ln K = A + B/T$

Metal	ln K_W constants ^a		Ref.	ln K_S constants ^b		Ref
	A ₁	B ₁		A ₂	B ₂	
V	-2.437	-2692	2,7,8	-14.181	3490	8
Ti	-1.272	792	8	-13.016	5390	8
Cr	-3.29	-8170	7	-	-	
Y	-2.295	4538	2,7,8	-2.295	10720	9
Zr	-3.411	1358	8	-15.155	7540	8
Li	-	-		-11.744	6182	6

^aThese values of A₁ and B₁ result in a distribution coefficient in wt units.

^bThese values of A₂ and B₂ result in a Sievert's Constant in units of wt fraction torr^{-1/2}.

Table 2. Calibration of Hydrogen in Loop via Hydrogen Content in Yttrium Specimens Exposed to Lithium

Spec. No.	Exposure Temp (°C)	Cold Trap Temp(°C)	H (wt%) in Yttrium	Kw ^a	H(wppm) in Lithium
Y8	408	221	1.00 ± .27	78.94	127
Y9	422	230	0.98 ± .24	69.03	142
Y15	482	210	0.48 ± .01	41.08	117
Y11	482	220	0.38 ± .06	41.08	92
Y16	482	210	.41	41.08	100
Y60	538	215	.21	27.13	77
Y61	538	215	.32	27.13	118

^a Calculated from distribution coefficient equations in Table 2.

VII. FIGURE CAPTIONS

FIG. 1. Solubility of Hydrogen in Liquid Lithium.

FIG. 2. Time Dependent Concentration of Hydrogen in Lithium in the FFTL-3 Forced-Circulation Loop.

FIG. 3. Temperature Dependence of Equilibrium Distribution Coefficients for Hydrogen between Selected Vanadium Alloys and Lithium.

FIG. 4. Effect of Lithium Exposure on Hydrogen Concentration in Vanadium Alloys.

FIG. 5. Hydrogen Evolution from Vanadium Alloys Before and After Exposure to Liquid Lithium at 500° C: (a) V-15Cr-5Ti, (b) V-3Ti-0.5Si.

Fig.